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E.M.R. CUPOLA YIELD STUDY

FINAL REPORT - JANUARY 29, 1985

P.R. #8829.4 Rev.1

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HATCH ASSOCIATES

21 St. Clair Ave. East
Toronto, Ontario M4T 1L9, Canada
Telephone (416) 962-6350
Telex 065-24315

March 28, 1985

Foundry Section
Physical Metallurgy Laboratories
Canmet
568 Booth Street
Ottawa, Ontario
K1A 0G1

Attention: R. Wards

Dear Dick:

Re: Contract File No. 03SQ-23440-3-9181
Cupola Metallurgy Program

Enclosed please find ten (10) copies of the revised version of our final report (P.R. 8829.4 Rev.1) on the above project. I have not re-submitted the appendix as there were no changes to this portion of the report.

Yours sincerely,

S.V. McMaster, P. Eng.

HATCH ASSOCIATES LTD.

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PROJECT REPORT

P.R. #8829.4
File #8829.2

January 29, 1985

DSS CONTRACT FILE #03SQ-23440-3-9181

E.M.R. CUPOLA YIELD STUDY

FINAL REPORT - JANUARY 29, 1985

1.0 INTRODUCTION AND SUMMARY

The final phase of the Cupola Metallurgical Yield project including collection and analysis of the final field data, is complete. The objective of achieving a better understanding of the factors which govern the yield of alloys in a cupola has been met. The results of this work has the potential, if applied properly, to provide significant benefits to foundry cupola operations.

The initial phase of the project was to develop background data on the yield of Silicon, Manganese and Carbon in a cupola. To accomplish this four foundries were requested to participate in the testwork required to develop a database. These foundries were visited and comprehensive measurements made in order to allow the development of a detailed mass balance for the alloys under investigation. Analysis of the material balance was aimed at identifying ways to improve alloy yield, principally of silicon and manganese. The data and results of the initial field work are presented in HA Phase II Report #8829-3 August 30, 1984.

Two specific areas were identified in Phase II of the project that were felt to have sufficient potential to warrant further investigation in the third and final phase of the project. These involved the yield of silicon at a foundry producing ductile iron (Foundry A) and the yield of manganese in a foundry producing large gray iron castings (Foundry B). Owing to similarities between the cupola operations, the intent was to be able to draw conclusions from the final testwork that would directly benefit the two foundries involved and also be applicable to cupola operations in general. It was felt that some useful information could be developed and made available to the Canadian foundry industry, specifically involving cupola operating practices.

If you disagree with any information contained herein, please advise immediately.

1.0 INTRODUCTION AND SUMMARY (Cont'd)

Changes in operating practice to improve silicon yield at foundry A met with very positive results, showing an improvement in silicon yield on the order of 15%. Similarly improvements in manganese yield at foundry B were observed but were not as dramatic.

Development of a thermodynamic model to predict the yield behaviour in a cupola has met with limited success. The theoretical basis for the model has been established. After the model had been developed it became apparent that the mathematical solution to the system of differential equations was extremely complex. Considerable effort was then expended in order to:

(a) Attempt to simplify the non linear differential equations in order to arrive at a unique solution.

(b) Investigate the mathematical divergence in order to gain a better understanding of how the problem could be solved.

This work is presented in Appendix 1. The result of rigorous analysis of the problem led to the conclusion the solution was in fact path dependent (in this case the path being the vertical solids temperature profile in the cupola). Recommendations to ultimately achieve a solution to this complex problem are presented.

The objectives of the study have been achieved. A major step has been made in the development of a thermodynamic model of a cupola operation. It is felt that the work done in developing and understanding of the problem would now allow a test program to be designed that would provide information to allow solution of the governing differential equation.

In more concrete terms the operating changes developed to improve silicon yield have been adopted by foundry A with an estimated annual savings in coke, limestone and silicon estimated at $200,000 per year.

2.0 EVALUATION OF IMPROVEMENT IN SILICON AND MANGANESE YIELD

2.1 Silicon Recovery

The main route to an improvement in silicon recovery at foundry A was used to reduce the slag volume (lower the amount of limestone addition) to result in a slag that would contain the silica and alumina component of the coke and only enough limestone to yield a slag basicity on the order of 1.0 or slightly less. The major concern of an increase in sulfur pickup with the reduced slag volume was not evident, a slight increase in tap sulfur levels from 0.09 to 0.10 percent was not considered detrimental to iron quality.

Silicon enters the cupola in two forms, as silicon metal (in the scrap or ferrosilicon) and as $Si0_2$ (in the coke and limestone). Table 1 compares the silicon balance of the old pratice with the modified charge makeup.

Table 1: Foundry A - Silicon Balance

	Old Practice		New Practice	
	(%)	(kg/hr)	(%)	(kg/hr)
Charge:				
- In scrap	3.5	(12.1)	6.5	(11.8)
- Coke ash	6.1	(21.1)	9.3	(16.9)
- Limestone	1.5	(5.2)	2.6	(4.7)
- Ferrosilicon	88.9	(308.1)	81.6	(148.3)
Tap:				
- In iron	67.6	(234.2)	62.0	(112.7)
- In slag	32.4	(112.3)	38.0	(69.1)

Although the apparent yield is lower, the form of silicon addition should be considered. This is best evaluated by comparing the amount of silicon metal which is oxidized in the slag (i.e. assuming that all silicon entering as oxide must leave as oxide). This comparison is shown in Table 2.

Table 2: Silicon Oxidation

	Old Practice Kg/hr	New Practice Kg/hr
Charge S_i	320.2	160.1
Oxidized	72.9	47.4
% Oxidized	22.8%	29.6%
S_i Recovery (Spout S_i) (Charge S_i)	73.1%	70.4%

2.1 Silicon Recovery (Cont'd)

The initial testwork at foundry A indicated a slag basicity of 1.33, operating with 110 lbs. of limestone per charge. The considerable reduction in limestone addition to 70 lbs per charge) would be expected to provide a substantial reduction in basicity. This was not the case as the basicity fell to only 1.21 as a result of the reduction in charged limestone. Although this unit is a water cooled cupola there is some refractory material, subject to attack in the well and slag hole area. Observation indicates that there is considerably less erosion of the patch materials used in the cupola lining (composed primarily of $Si0_2$). This reduced erosion, coupled with the lower amount of charged silicon results in a slag of essentially the same composition but produced in significantly less volume.

Similar studies (1) done concerning the relation between charge or base silicon would indicate an improvement in the percentage recovery of silicon for a lower base silicon charge. This work appears to consider base silicon as silicon contained in the scrap charge but not the amount added as ferro-alloy. The scrap charge at Foundry A is primarily steel scrap and has not changed appreciably in the period of this testwork (a slightly lower proportion of cast iron scrap is now charged). This would indicate that addition of ferrosilicon especially when a low silicon bearing scrap mix is used is not a desirable method of achieving a higher Carbon Equivalent. The basis for this statement is the apparent low silicon recovery achieved when the charge silicon is added in concentrated form such as 50% ferro-silicon.

Table 3: Silicon Recovery

Foundry	A	B	C	D
Charge Silicon				
- Scrap (kg/hr)	12.1	173.6	106.6	93.8
- $FeSi$ (kg/hr)	308.1	83.1	4.3	16.3
- SiC (kg/hr)	--	--	66.4	--
Recovery (%)	73.1	86.3	89.9	83.0

When compared to carbon on a weight basis silicon only contributes one third of the value to the carbon equivalent. In general this would indicate that if the cost advantage of charging steel scrap is persued high carbon equivalent value should be sought through carbon pickup from the coke bed in the cupola and not by addition of more expensive ferrosilicon.

2.1 Silicon Recovery (Cont'd.)

This is substantiated, if one considers Levi's equation for carbon pick-up.

$C_{spout} = \frac{1}{2}C_{charge} - \frac{1}{2}(S_i + P)_{spout}$ which would indicate that better carbon pick-up could be expected for lower spout silicon levels.

This appears feasible when the carbon pickup in Foundry A is considered, shown in Table 4.

Table 4: Carbon Pickup Foundry A

	Old Practice	New Practice
Base carbon (scrap)	0.68	0.30
Tap Carbon	3.29	3.28
Carbon Pickup	2.61	2.98
Carbon Equivalent	3.99	3.60

The net loss in carbon equivalent of 9.7% is low enough that a suitable graphitizing effect can be achieved by innoculation with ferrosilicon in the ladle to increase Carbon Equivalent. This has two major advantages, the recovery of post silicon addition approaches 100% which is a significant improvement over the 60-70% which appears to be the maximum that can be attained in the cupola. The second advantage is higher carbon pick-up in the cupola, due to lower spout silicon values. Better cupola silicon recovery may be possible if more expensive, higher silicon scrap is used, but this may not be cost effective.

It has been well established that the graphitizing effect of innoculation is transient and that the best results are achieved when the addition is made as late as possible before pouring (2). This would tend to reinforce a recommendation to minimize silicon addition to the cupola, optimize carbon pick-up and add a silicon alloy (75% or greater S_i) as late as possible before pouring. It is felt that this operating approach has potential for wide application in cupola operations. It must be noted that other operating constraints, such as temperature or shrinkage may limit the amount of post silicon addition. The heat of

2.1 Silicon Recovery (Cont'd.)

solution of pure silicon is nearly equal to the latent heat of fusion and temperature loss on addition is a result of iron units contained in the alloy. Adding high purity silicon (i.e. 85% feS_1) can increase the total post addition possible, if iron temperature is a limiting factor.

2.2 Manganese Recovery

The studies of the factors governing the recovery of manganese were not as conclusive as was the case for yield of silicon. A considerable reduction in the amount of limestone being charged to the cupola was implemented after the inital testwork was carried out at Foundry B. The change in slag basicity as a result of lower limestone addition was to lower basicity from 1.06 to 0.88, the apparent improvement in manganese recovery was 3.2% from 81.6% to 84.8%. This would indicate that manganese recovery is not highly dependent on slag basicity and that reducing slag volume may result in a marginal improvement in manganese recovery.

By reducing the total manganese lost to the slag (from 18.5% to 14.8% of total manganese charged) shifts the ratio of manganese contained in scrap to charged as ferro manganese from 0.40 to 0.56. Charging a greater proportion of the manganese in a dilute form (scrap composite of 0.3% compared to 66% in ferro manganese) may outweigh the effect of the reduced slag basicity. The manganese balance for Foundry B is shown in Table 5.

Table 5: Foundry B - Manganese Balance

		Old Practice (%) (kg/hr)	New Practice (%) (kg/hr)
Charge:	- in scrap	28.3 (65.2)	38.7 (74.5)
	- ferro manganese	71.7 (165.1)	61.3 (117.9)
Tap:	- in iron	81.5 (187.7)	85.4 (164.4)
	- in slag	18.5 (42.6)	14.6 (28.1)
Maganese Recovery (%)		81.5	85.4

3.0 OPTIMIZATION OF ALLOY RECOVERY IN A CUPOLA

It is evident that the outcome of this work can be applied in general terms to almost any cupola used for the production of gray or ductile cast iron. The recovery of manganese would appear to depend on slag volume to a greater extent than that of silicon, given the lower tendency of manganese to oxidize (as compared to silicon) would tend to support this. The observed yields of manganese of 85 - 100% in the four cupolas studied coupled with the total lower amount of manganese required (0.4 - 0.7% for most ductile/gray iron)[2] does not provide a great incentive to reduce manganese losses in the cupola. Charging manganese in more dilute form has obvious advantages in terms of recovery, however the room for improvement is not sufficient to outweigh the increased cost of higher quality scrap. Specifically the cost of adding say 0.5 percent of manganese at an 80% yield fator is on the order of $6.30 per tonne of iron compared to a differential as high as $100 per tonne for pig iron (high manganese) versus steel scrap. There would not appear to be any advantage in terms of innoculation effect, of adding manganese outside the cupola as is the case for silicon addition, if a duplexing operation is considered an improvement in the recovery of manganese to levels of 95 - 100% could be expected, when manganese is added outside the cupola.

Silicon losses observed and reported in the literature [1] are higher than observed manganese losses, this coupled with the higher amounts required for ductile or gray iron of 1.25 - 2.75% [2] would indicate a greater incentive for improving silicon recovery. As with manganese however the cost of adding say 1.5 percent of silicon at a recovery of 60% is on the order of $29 per tonne of iron. This is significantly more than the cost of manganese but is still not enough to offset the cost of a higher quality scrap charge. Unlike manganese there are well established benefits, in addition to improved recovery, to add silicon outside the cupola. Depending on specific foundry conditions there may be limits to the amount of post silicon addition possible.

The key recommendation derived from this study is to minimize slag volume by reducing the limestone charged to the cupola, within the limits necessary to maintain required slag basicity and fluidity. In order to maintain similar basicity with a reduced limestone charge would indicate lower ferrosilicon additions, to the charge. The key direct benefit derived from lower limestone addition is a proportional reduction in the coke required to provide energy for calcination and melting of the limestone. Two other, less significant benefits include the possibility of slightly improved manganese yield and reduced consumption of refractory patch material used in the cupola. The percent yield (in the cupola) would not be expected to change appreciably provided the ferro silicon charged to the cupola is reduced. The lower tap silicon level does not have a dramatic effect on carbon equivalent value and can be compensated for by addition of silicon to the receiver or ladle, within limits of temperature loss and shrinkage of castings.

4.0 THERMODYNAMIC MODEL

An attempt was made to mathematically model both the thermal and kinetic factors which influence the recovery of carbon, silicon, and manganese in an iron melting cupola. In concept, the model was quite simple, consisting of heat and mass transfer between the gas and solid phases (Note: in this case the term solid includes the liquid metal and slag which are formed in the lower regions of the cupola). However, the actual system of equations involved in the transfer operations turned out to be extremely complex. Equation 1, shown below, is the governing differential equation for the transfer of heat between the gas and tne sold phases. The derivation of this equation is given in Appendix 1. Development of the equation's also required that some simplifying assumptions be made. These assumptions are presented in Appendix 2.

$$\left(\frac{dH_g}{dT_g} - \frac{dH_s}{dT_g} - \frac{dH_l}{dT_g} - \frac{dH_R}{dT_g} \right) \frac{dT_g}{dZ}$$

$$= \left(\frac{-dH_g}{dT_s} + \frac{dH_s}{dT_s} + \frac{dH_l}{dT_s} + \frac{dH_R}{dT_s} \right) \frac{dT_s}{dZ} \qquad \text{i}$$

4.1 Development of the Terms in the Equation

Where: $\frac{dH_g}{dT_g}$ is the rate of change in gas enthalphy with gas temperature. This can be represented by two terms: one representing the influence of direct temperature changes in the gas ($M_g C_{pmg}$) and the other ($H_{mg} T_g$) dM_g/dZ) representing the fact that there is a change in the number of moles of gas taking place due to tne chemical reactions. These two componenets can be summed to give the total influence of changes in the gas temperature on the enthalpy of the gas.

$$(M_g C_{pmg} + H_{mg} (T_g)\ dM_g/dZ)\ t = dH_g/dT_g \qquad 2$$

M_g = molar flowrate of the gas
C_{pmg} = molar specific heat of the gas mixture evaluated at T_g
H_{mg} (T_g) = molar enthalpy content of the gas evaluated at T_g
dM_g/dZ = the rate of change in molar flowrate as a function of vertical position
T_g = the gas temperature at any position in the cupola
t = the time step.

$\frac{dH_s}{dT_g}$ is the rate of change in solids enthalpy with gas temperature. This term can also be represented by two terms; one representing heat transfer from the gas to the solids ($h_{gs}A$) and the other ($T_g \frac{d}{dT_g} (h_{gs}A)$) representing the change in the heat transfer coefficient due to changes in the gas temperature.

h_{gs} = the gas-solids heat transfer coefficient
A = the area of the cupola
T_g = the gas temperature at any position in the cupola
$\frac{d}{dT_g} (h_{gs}A)$ = the variation of the heat transfer coeffient with gas temperature
= Zero for a constant gas-solids heat transfer coefficient and area

Thus combining the terms yield the following equation for the rate of change of the solids enthalpy.

$$\frac{dH_s}{dT_g} = (h_g sA + T_g \frac{d}{dT_g} (h_{gs}A))\ t \qquad __3$$

$\frac{dH_l}{dT_g}$ is tne rate of change of enthalpy loss with gas temperature. The loss term can also be represented by two terms; the first ($h_{gw}A_w$) represents the direct influence of gas temperature on the loss of enthalpy and the second ($T_g\ d/dT_g(h_{gw}A_w)$) represents tne influence of the gas temperature on the loss heat transfer coefficient.

$$\frac{dH_l}{dT_g} = (h_{gw}A_w + T_g\ d/dT_g\ (h_{gw}A_w))t \qquad __4$$

h_{gw} = the gas-wall heat transfer coefficient
A_w = the area of the cupola wall
T_g = the gas temerature at any position in the cupola
$\frac{d}{dT_g} (h_{gw}A_w)$ = the effect of gas temperature on wall heat transfer coefficient
= Zero for constant gas-wall heat transfer coefficient and area.

$\frac{dH_R}{dT_g}$ is the rate of change of reaction enthalpy with gas temperature. Like the other terms, this consists of two components; the first ($\sum_{j=i}^{9} (n_j(Cp_{zgp_j} - Cp_{gR}))$) the result of changes in the reaction enthalpy due to the temperature gradient, while the second ($\sum_{j=1}^{9} (HREAX_j \frac{dn_j}{dT_g})$) result of the change in reaction rate due to the thermal gradient.

$$\frac{dH_R}{dT_g} = t\left(\sum_{j=1}^{9} (n_j(Cp_{gp_j} - Cp_{gR_j})) + \sum_{j=3}^{4} (HREAX_j \frac{d}{dT_g}\right) \quad \text{—5}$$

n_j = the reaction rate of reaction j (j=1,2,3,...9)

Cp_{gR_j} = specific heat of the gaseous reactants for reaction j

Cp_{gp_j} = specific heat of the gaseous products for reaction j

$HREAX_j$ = the enthalpy of reaction j at the reaction temperature

$\frac{dn_j}{dT_g}$ = the influence of the gas temperature on the reaction rate of reaction j

N.B. The cupola model has been set up using 10 discrete horizontal slices to allow finite solution of the change in reaction enthalpy.

(Note: Reactions 1 & 2 have reaction kinetics which are independant of the gas temperature.)

$\frac{dH_g}{dT_s}$ is the rate of change in gas enthalpy with solids temperature. This is the reverse of the second term (dH_s/dT_g), so that the enthalpy transferred from the gas to the solids results in a lowering of the gas temperature.

$\frac{dH_s}{dT_s}$ is the rate of change in solids enthalpy with solids temperature. This is also a two term function; the first ($M_s Cp_{ms}$) is the direct result of the change in the gas temperature, while the second ($H_{ms}(T_s) \frac{dM_s}{dZ}$) is the result of a change in the number of moles of gas

$$\frac{dH_S}{dT_S} = t(M_S Cp_{ms} + H_{ms}(T_S)\frac{dM_S}{dZ}) \quad \text{---6}$$

M_S = the molar flowrate of solids in the cupola
Cp_{ms} = the molar specific heat of the solids at T_S
$H_{ms}(T_S)$ = the molar enthalpy content of the solids at T_S
$\frac{dM}{dZ}$ = the rate of change in the molar flowrae of the solids with vertical position.
T_S = the solids temperature at any point in the cupola.

$\frac{dH_I}{dT_S}$ is the rate of change in enthalpy loss with solids temperature. Since most of the energy is lost from the gas phase, this term is assumed to be zero.

$\frac{dH_R}{dT_S}$ is the rate of change in reaction enthalpy with solids temperature. This is also a two term function; the first term $(\sum_{j=1}^{9} (n_j(Cp_{sp_j} - Cp_{sR_j}))$ is the result of the change in the number of moles of the solid, while the second term $(\sum_{j=i}^{2} (HREAX_j \frac{dn_j}{dT_S}))$ is the result in the change in the nature of the solid material.

n_j = the rate of reaction for reaction j
Cp_{sp_j} = the specific heat of the solid products for reaction j evaluated at the solids temperature.
Cp_{sR_j} = the specific heat of the solid reactants for reaction j.
$HREAX_j$ = the heat of reaction for reaction j at the reaction temperature.

$\frac{dnj}{dT_S}$ = the influence of the solids temperature on the rate of reaction j

$$\frac{dH_R}{dT_S} = \sum_{j=1}^{9} (n_j(Cp_{sp_j} - Cp_{sR_j})) + \sum_{j=1}^{2} HREAX_j \frac{dn_j}{dT_S} \quad \text{---7}$$

$\frac{dT_S}{d_Z}$ - is the rate of change in gas temperature with vertical distance (Z)

$\frac{dT_S}{d}$ - is the rate of change of solids temperature with vertical distance (Z)

The nature of this equation makes the use of a numerical solution technique imperative. A one-dimensional finite difference scheme was selected as the method which seemed to yield the best balance between the information available and the degree of complexity required to produce a solution. The finite difference technique divides the cupola into a number of horizontal slices, or nodes, through the cupola. In each of these nodes the solids temperature is assumed to be constant, as is the gas phase temperature. This type of technique has been successfully used in the modelling of iron blast furnaces by several workers (3,4,5). It seemed reasonable to assume that if blast furnaces could be modelled, the seemingly simpler case of the cupola should represent no real new problem. This turned out not to be the case. In the first place, blast furnaces seem to operate much closer to thermodynamic equilibrium than do cupolas. Secondly, much more information is available about the internal workings of blast furnaces than is the case for cupolas.

4.2 Model Structure

As mentioned earlier, the model consists of two major parts; heat transfer and kinetics.

These two processes are closely related since the reactions either release or consume heat. Furthermore, the kinetics of the reactions are strongly temperature dependent. Thus, the heat transfer and the reaction kinetics must be handled simultaneously. Given the two temperatures and the solid and gas phase compositions, the rates of the reactions within a given slice can be calculated. Once the rates of the reactions are known, then the amounts of energy consumed and/or produced can be calculated. Given this information as well as the energy balances on the gas and solids, a new pair of temperatures can be calculated. These steps are repeated for every node in the cupola until there are no further changes in the gas and solids temperatures.

There are seven major chemical reactions which must be considered in the cupola, these are:

(1) $CaCO_3 = CO_2 + CaO$

(2) $MgCO_3 = CO_2 + MgO$

(3) $O_2 + C = CO_2$

(4) $CO_2 + C = 2CO$

(5) $H_2O + C = CO + H_2$

(6) $Mn + CO_2 = CO + MnO$

(7) $Si + 2CO_2 = 2CO + SiO_2$

Of these, reactions (3) and (7) are exothermic, and the others are endothermic.

The calculations are performed in the order shown in the flow chart in Fig. 1. These ten subprograms will be explained later.

4.3 Heat Transfer

Since the prime function of the cupola is the production of liquid iron and the rate of heat transfer to the iron controls the rate of production the heat transfer from the gas phase where combustion is taking place to the charge is of paramount importance. In this case, the dominant factor influencing the transfer of heat is the convection occuring between the rising gas and the descending burden. In addition to convection, some radiation and conduction are also taking place. However, the implicit goal of a counter-current reactor such as a cupola is to reduce the horizontal thermal gradients between the gas and the solid phases and those within these phases. Under these conditions, a lumped parameter approach to the heat transfer can be justified. The lumped parameter in this case would be the heat transfer coefficient (h) in equation 8.

$$E/A = n(T_g - T_s) \qquad 8$$

where E/A = the heat flux
h = heat transfer coefficient
T_g = gas temperature
T_s = solids temperature

Ideally, this lumped heat transfer coefficient would be obtained by making measurement in a production cupola. However, this information is not available so the heat transfer coefficient must be obtained from other packed-bed counter-current reactors. Equation 9 gives a heat transfer coefficient for vertical packed-bed counter current reactors [6].

$$h_{gs} = 2.06\frac{PU_DC_p}{\epsilon} Pr^{-2/3}Re^{-0.575} \qquad 9$$

h_{gs} = gas/solids heat transfer coefficient
U_D = gas velocity in the empty cupola
P = gas density in the cupola
C_p = gas specific heat at termperature Tg
ϵ = the bed porosity in the cupola
P_r = the Prandtl number for the gas in the cupola
Re = the Reynolds number for the gas moving in the empty cupola.

This empirical equation was obtained by the analysis of data from a number of industrial processes, ranging from gas adsorption towers to blast furnaces. This equation takes a number of properties of these processes into account. For the case of the cupola, some of the more significant of these are particle size, gas velocity, and the thermophysical properties of the gas (viscosity, specific heat etc.). These are the variables which help to characterize a process since these depend strongly on the materials being input into the process and the histroy of the materials at any point in the process.

The program calculates the thermal profile in the cupola in a number of stages because of the strong interrelationship between the transfer of heat and the rates of the chemical reactions. Firstly, the solids temperatures are calculated (SOLTMP) from the old solids temperatures and the gas temperatures. Then the amounts that each reaction proceeds in a given node is calculated using the new solids temperatures and the old gas temperatures. Given these changes, the changes in the solids and gas composition is calculated (GASCOM). Finally, the new gas temperature is calculated (TGASCH) given the energies released/consumed and the new gas temperature. The new gas and solid temperatures are compared with the old temperatures (COMPARE), if either temperature in any node is more that 10% different from the old temperature, the calculation is repeated.

4.4 Kinetics

The kinetics of most of the reactions, as in many high-temperature heterogeneous reactions, are controlled by the rate of transfer of gaseous reactants to the interface. The two exceptions are the two calcination reactions (reactions 1 and 2).

4.5 Calcination

Turkdogan (7) found that the calcination of limestone is dependent on the rate of heat transferred to the unreacted limestone. This means that both the size of the limestone and the prior thermal history of the limestone are important in determining the rate of limestone calcination. There are two parameters which are required to calculate the fraction calcined in a given size range, these are; the time required to initiate calcination and the fraction of limestone previously calcined. The incubation period depends on the type of material being calcined, magnesium carbonate calcines at a lower temperature than calcium carbonate. The fraction previously calcined depends on the thermal history of the limestone.

Turkdogans work gave:

for CaCO (CALC)

$$0.1044\left(t - 1.25 \times 10^5 \exp\left(-0.00757 T_s\right)\right) = 3 - 2F - 3(1 - F)^{2/3} \qquad (10)$$

t = time spent at temperature T_s
T_s - solids temperature
F = fraction of limestone calcined at T_s

for MgCO (CALM)

$$0.1044\left(t - 1.25 \times 10^5 \exp\left(-0.025 T_s\right)\right) = 3 - 2F - 3(1-F)^{2/3} \qquad (11)$$

Note: Newton's method is used to solve for F at each temperature for both CALC and CALM.

4.6 Water Gas Reaction

The water gas reaction (WG), reaction 5, occurs very rapidly since water vapour is unstable under the conditions found in the hearth of a cupola. Iguchi (8) found that for blast furnaces, the amount of water vapour remaining after the gas travelled a given distance depended only on the initial concentration in the gas and the time taken for the gas to travel that distance. Equation 12 is the relationship that he postulated for this reaction.

$$H_2 = H_2O \left(2 - \mathrm{Exp}(-3. * dZ)\right) \qquad (12)$$

where H_2 = the number of moles of hydrogen (and CO) produced in a node
H_2O = the number of moles of water vapour entering the node
dZ = the height of the node

4.7 Combustion

Similarly to the water gas reaction, the relationship between oxygen and carbon to form carbon dioxide (CO2FOR) depends only on the initial oxygen concentration and the time taken to travel the distance (8). In addition, the coke particle diameter enters into the equation.

$$O_{2C} = O_{2A} \exp \frac{-0.35 * DZ}{d_C * E} \qquad (13)$$

where O_{2C} = moles of oxygen consumed in the zone
O_{2A} = moles of oxygen available in the zone
dZ = the height of the zone
d_C = the diameter of the coke particles
E = the bed porsity

4.8 Bouduard Reaction

The reaction between carbon dioxide and carbon to produce carbon monoxide (COFORM) is dependent on the inital carbon dioxide concentration, the carbon monoxide concentration, and the gas phase temperature (8).

$$F_{CO} = \frac{C_A A P_{CO_2}}{(1 + BP_{CO} + CP_{CO_2})}$$

wnere F_{CO} is the rate of CO formation (moles/min)
P_{CO_2} is the partial pressure of CO2 in the gas
P_{CO} is the partial pressure of CO in the gas
$A = 1.00 \times 10^5 \exp(-6100/RT_g)$
$B = 4.00 \times 10^4 \exp(40300/RT_g)$
$C = 3.16 \times 10^{-2} \exp(6100/RT_g)$
R is the gas constant
T_g is the gas temperature.

4.9 Si, C, and Mn Loss Reactions

The three reactions involving the loss of alloying elements from solution are complex. First of all, it is unlikely that significant losses of alloying additions would occur prior to the melting of the iron. Secondly, no information is available on the kinetics of these reactions under the conditions found in a cupola. Therefore, it is assumed that the rate of oxidation of these elements depends on the oxygen potential at the interface and the rate of transfer of oxidizing gas, in this case carbon dioxide, to the interface. Using an analogy between heat and mass transfer, a mass transfer coefficient, k, can be arrived at from equation 14.

$$k = 2.06 \frac{U_D}{E} S_c^{-2/3} R_e^{-0.575} \qquad 14$$

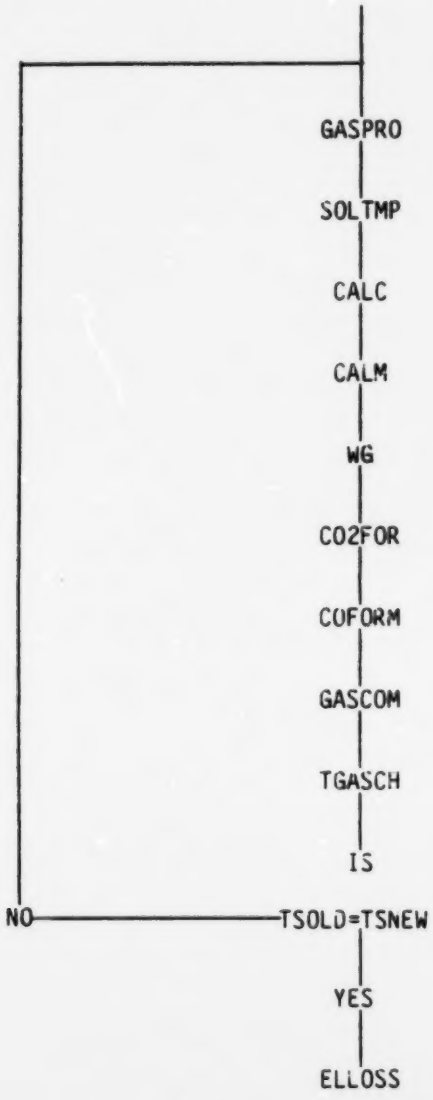
k is the mass transfer coefficient
U_D is the gas velocity in the empty cupola
S_c is the Schmidt number
R_e is the Reynold's number based on the empty cupola.
E is the bed porosity.

Given this, the amount of the element reacted can be calculated from equation 15.

$$\frac{n_i}{A} = \frac{kP_T}{RT_g} (P^b_{CO_2} - P^*_{CO_2}) \qquad 15$$

where $\frac{n_i}{A}$ is the molar flux of element i
k is the mass transfer coefficient
R is the gas constant
P_T is the total gas pressure in the system
T_g is the gas constant
$P^b_{CO_2}$ is the bulk partial pressure of CO_2
$P^*_{CO_2}$ is the equilibrium partial pressure of CO_2 at the gas/solids interface.

Since the amount of these reactions is relatively small and unlikely to affect either the temperature profile or the gas composition to great extent, these reactions are handled after the main loop. After the steady state temperature profile has been achieved, the program then calculates the fractions of the elements consumed by these reactions. At this point the energy released/consumed is known and the temperature and composition profiles are then recalculated.



GASPRO calculates the gas properties as a function of temperature.
SOLTMP calculates the new solids temperature
CALC and CALM calculate the calcination of calcium and magnesium carbonate respectively
WG calculates the kinetics of the water-gas shift reaction
CO2FOR calculates the formation of CO_2 from combustion
COFORM calculates the kinetics of the Bouduard reaction
TGASCH calculates the new gas temperature
ELLOS calculates the loss of Si, Mn, and C

TSOLD is the old solids temperature, while TSNEW is the new solids temperature.

Figure I: Flow Chart for Thermodynamic Model

5.0 RECOMMENDATIONS

A better understanding of the factors which govern the yield of alloys in a cupola has been achieved however the nature of a cupola operation makes analysis of the many effects of changing operating parameters difficult. The survey of four foundries has served to identify areas in which improvements are possible, and some definite gains have been made.

The next logical step in a program to assist Canadian foundries optimize their cupola practice would be a comprehensive data logging and monitoring program on one cupola.

The objective of such a program would be to eliminate the effect of day to day changes in uncontrollable variables such as humidity, variation in scrap composition etc. by employing automatic, continuous measurement of operating parameters.

Means are available to measure the vertical temperature profile in an operating cupola which would provide the necessary data to allow solution the thermodynamic model developed in this program. Through instrumentation of a cupola, the cupola model could be utilized as the basis for a sophisticated process control system that could evolve directly from a program of instrumenting and monitoring an existing unit.

Implementation of state of the art technology in terms of process control to optimize blast rate, and iron chemistry would be a major innovation to the operation of cupola's and is certainly a worthwhile goal.

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